Imidazole-containing chitosan derivative: a new synthetic approach and sorption properties

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A novel method for the synthesis of a hetaryl-containing chelate amino polymer, namely, *N*-(4(5)-imidazolylmethyl)chitosan (IMC), with a degree of substitution up to 0.3 was proposed. The "synthesis in gel" approach involves direct substitution of the hydroxyl group in 4(5)-imidazolylmethanol. The structures of these polymers were confirmed by ^{1}H NMR data. For sorption studies, IMC samples were crosslinked with epichlorohydrin and diglycidyl ethers of ethylene glycol and diethylene glycol. The degrees of swelling and sorption properties of the polymers largely depend on the crosslinking agent and the degree of crosslinking. The sorption capacities of IMC for Au^{III}, Pt^{IV}, and Pd^{II} ions are higher than those of the nonmodified polymer. The extraction of noble metal ions from chloride solutions becomes more selective with increasing degree of crosslinking. The sorption capacity of IMC for Co^{II} and Ni^{II} ions is higher than those of chitosan and its known N-heterocyclic derivatives.

Key words: chitosan, *N*-(4(5)-imidazolylmethyl)chitosan, sorbent; gold(III), platinum(IV), palladium(II), silver(I), copper(II), cobalt(II), and nickel(II) ions.

Functionalization of polymers, including chitosan, is a useful tool for diversifying the practically important properties of well-known and accessible polymer materials and, consequently, extending their areas of application. Chitosan is an amino polymer commercially produced by deacetylation of naturally occurring chitin. The high reactivity of chitosan opens great scope for targeted chemical modification aimed at the preparation of polymers with new useful properties.[1—3]

Introduction of heteroaromatic fragments into the chitosan structure is known as an approach to considerable modification of the properties of the polymer as well as a route to new biologically active compounds, polyfunctional metal-containing materials, and materials for sorption and catalytic purposes.[4—18] Pyridine, thiophene, and imidazole have been reportedly employed as heteroaromatic radicals. For instance, *N*-(4- or 3-pyridylmethyl)-chitosan shows enhanced antibacterial properties[4—6] and chelating *N*-(2-pyridylmethyl)chitosan (PMC) has an increased sorption capacity and selectivity for copper(II) ions.[7,8] The sorption capacity of a polymer capable of forming a five-membered chelate ring has been found to be indeed three times that of a polymer containing the nonchelating 4-pyridyl group.[9] Derivatives of PMC are also highly active in the sorption of noble metal ions.[10—12] Chitosan modified with an electron-donating thienyl fragment compares with PMC in the sorption of noble metal ions.[12] Having the electron-donating N atom of the pyridine ring, both 4- and 2-pyridylmethyl derivatives can successfully be used as carriers for metal-containing materials.[13—16] Introduction of the imidazolyl fragment has been reported to increase the complexing ability of chitosan with respect to a cobalt(II) complex[17] and allow the synthesis of a polymer contributing to bone tissue formation.[18] In the former case, chitosan was modified with a chloromethyl derivative prepared from 4(5)-imidazolylmethanol; the degree of substitution (DS) was 0.75, the sorption value was 0.42 mmol of Co(II) g^{-1}.[17] In the latter case, DS was 0.30; however, the method for the synthesis of the polymer was not described.[18]

Currently available data on the synthesis and sorption properties of imidazole-containing chitosan derivatives are scarce, though such polymers are certainly promising for use in biomedicine, sorption, and catalysis. In the present work, we develop a new method for the synthesis of *N*-(4(5)-imidazolylmethyl)chitosan (IMC) and estimate its efficiency in the sorption of transition and noble metal ions depending on the nature of various crosslinking agents used.

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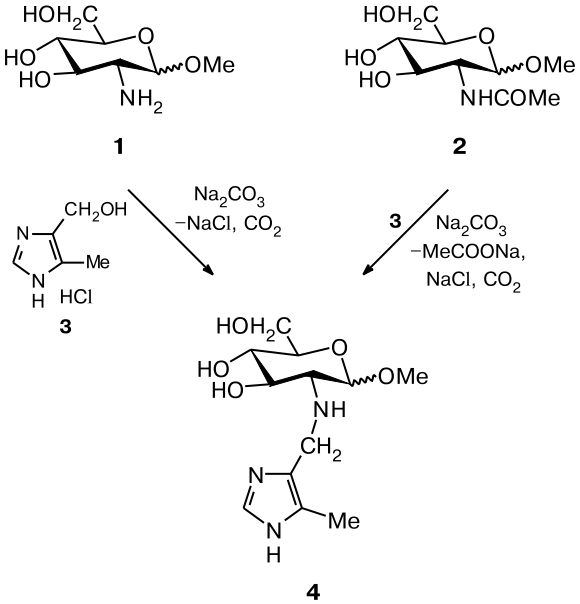
Results and Discussion

The only published route to IMC involves a reaction of chitosan with 4(5)-chloromethylimidazole in DMSO.[17] However, no proof of the polymer structure is provided. The drawbacks of this method for chitosan functionalization include the preliminary synthesis of the above reagent from the corresponding alcohol and the irreproducible modification procedure. Repeatedly attempted reproduction of this procedure has not ensured the claimed product. Direct replacement of the hydroxyl group in 4(5)-imidazolylmethanol by a secondary amino group, also with participation of an amino alcohol, has been described earlier.[19] This reaction[19] occurs by nucleophilic elimination—addition favored by the aromatic system of imidazole. To improve the route to IMC by skipping the preliminary synthesis of 4(5)-chloromethylimidazole from the corresponding alcohol, we proposed to use a reaction of chitosan with 4(5)-imidazolylmethanol.

First, we estimated the reactivity of the chitosan monomer in this transformation, using methyl 2-amino-2-deoxy-α,β-D-glucopyranoside (**1**) as a model reagent (Scheme 1). The conversion (93%) was determined from the integral intensity ratio of the ^{1}H NMR signals for the methylene groups bound to the aromatic ring in the starting reagent (δ 4.58) and the reaction product (δ 3.57).

Scheme 1



The spectrum of product **4** also exhibits signals at δ 4.75 for the H(1) atom of the substituted glucopyranose ring in place of the corresponding signal at δ 4.58 for the unsubstituted glucopyranose ring. Therefore, amino alcohol **1** proved to be highly reactive in this transformation. To find out whether an *N*-acetylated amino group can be involved in this reaction, we carried out a reaction of 4-methyl-5-imidazolylmethanol (**3**) with methyl 2-acetamido-2-deoxy-α,β-D-glucopyranoside (**2**). According to ^{1}H NMR data, the hydroxyl group in compound **3** is not replaced by the acetamide group. Under these conditions, *N*-acetylglucosamine undergoes deacetylation followed by the formation of the same product methyl 2-(4-methyl-5-imidazolylmethyl)amino-2-deoxy-α,β-D-glucopyranoside (**4**) (see Scheme 1). Apparently, the deacetylation under mild conditions is favored by the presence of the imidazole derivative, which is known to catalyze hydrolytic reactions.[20]

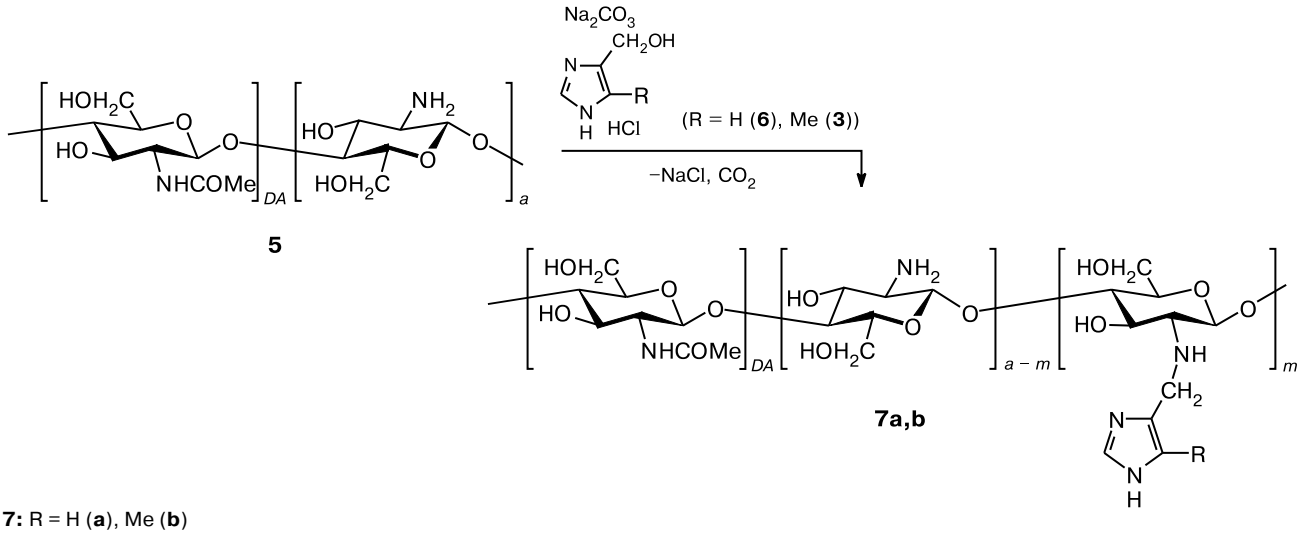
Earlier, we have demonstrated that chitosan can efficiently be modified under the "synthesis in gel" conditions *via* both nucleophilic addition[21–24] and nucleophilic substitution reactions.[25] Here we used the gel technology of polymer-analogous transformations to carry out reactions of chitosan (**5**) with 4(5)-imidazolylmethanol (**6**) and 4-methyl-5-imidazolylmethanol (**3**) (Scheme 2).

The IR spectra of products **7a,b** show a new absorption band at 1499 cm^{-1} characteristic of imidazole derivatives. Subtracting the spectrum of chitosan **5** from that of product **7b**, we revealed a band at 1669 cm^{-1} masked by an intense band at 1651 cm^{-1} (NHCOMe) in the initial spectrum. Structures **7a**,**b** were determined by ^{1}H NMR spectroscopy in solution (Fig. 1). Earlier, the chemical shift of the signal for the H(1) atom has been found to vary with the substituent(s) replacing the H atom(s) of the amino group.[21,24,25] The knowledge of this variation was used in the present work. It turned out that chitosan **5** is much less reactive than low-molecular-weight model compound **1** (Table 1). The highest DS value we achieved was 0.3. The use of a greater excess of 4(5)-imidazolylmethanol (**6**) did not increase DS substantially. The course of the reaction depends on the gel concentration; however, such low conversions preclude us from making unambiguous conclusions about both the character and extent of the concentration effect and the reactivity difference between 4(5)-imidazolylmethanol (**6**) and 4-methyl-5-imidazolylmethanol (**3**).

Attempted promotion of this reaction with ultrasound proved to be ineffective. Nor did we observe any dramatic changes in the reactivity of chitosan (**5**) when inorganic bases were variable (see Table 1). Note that product **7b** obtained in the presence of an organic base has a lower DS. Further modification of product **7a** with a DS of 0.15 yielded no IMC with DS >0.3 as well.

For a series of IMC samples derived from *N*-(4(5)-imidazolylmethyl)chitosan **7b** with a DS of 0.23 by additional crosslinking with various agents, we studied their sorption properties in the extraction of noble and transition metal ions (Tables 2, 3). The sorption capacities of poorly substituted IMC for gold(III), platinum(IV), and palladium(II) ions are much lower than those of 2-pyridylethyl-containing chitosan derivatives (DS = 0.83) syn-

Scheme 2



7: R = H (**a**), Me (**b**)

thesized earlier;[24] nevertheless, they are appreciably higher than the sorption capacity of unsubstituted chitosan (see Tables 2, 3). The limiting sorption capacity for noble metal ions extracted from 0.1 and 1 *M* HCl decreases in the order $Au^{III} > Pd^{II} > Pt^{IV}$, which is typical of the majority of known N-containing sorbents.[26] The observed drop in the sorption capacity with an increase in the concentration of competing chloride ions in solution is characteristic of the anion-exchange mechanism of sorption of noble metal ions as chloro complexes on some N-containing sorbents, including chitosan.[24,27]

It should be noted that the sorption capacity of IMC derivatives varies with the crosslinking agent. Epichlorohydrin-crosslinked products have the highest limiting sorption capacities for noble metal ions extracted from 0.1 *M* HCl and for transition metal ions extracted from 1 *M* NH_4NO_3 (pH 5.5). According to elemental analysis data, this material has the lowest degree of crosslinking (5%) (*i.e.*, its structure is most flexible), which is confirmed by its highest degree of swelling (250% in 0.1 *M* HCl). For

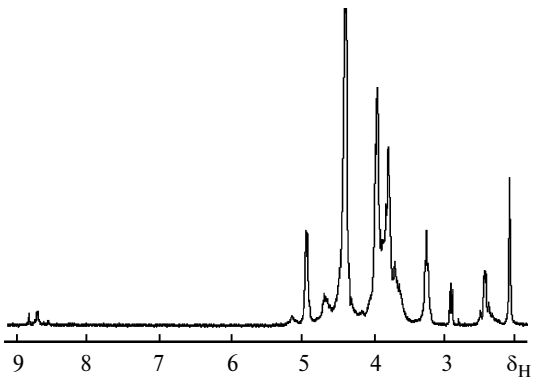


Fig. 1. ^{1}H NMR spectrum (400 MHz, δ) of product **7b** obtained by modification of chitosan (**5**) with 4-methylimidazol-5-ylmethanol (**3**) in D_2O/DCl: 2.06 (MeCO); 2.43 (Me, imidazole); 3.22—4.16 (CH_2, H(2), H(3), H(4), H(5), H(6)); 4.66 (H(1), GlcNHAc); 4.91 (H(1), $GlcNH_2$); 5.12 (H(1), GlcNHR); 8.72 (H, imidazole).

Table 1. Conditions and products of the reactions of chitosan **5** with 4(5)-imidazolylmethanols **6** and **3**

R	**6** or **3** : NH_2 (mole)	*t*/h (base)	Gel concentration (%)	DS of products **7a**,**b**
	T = 90 °C, Na_2CO_3 as a base			
H	1 : 1	45	7	0.13
		72	7	0.23
		84	12	0.30
	1.5 : 1	48	7	0.10
	2 : 1	48	7	0.08
Me	1 : 1	48	13	0.10
		48	4	0.18
		84	12	0.18
	1.5 : 1	48	7	0.10
	2 : 1	48	7	0.17
	Ultrasound (20 kHz), Na_2CO_3 as a base			
H	1 : 1	2/3	7	0
Me	1 : 1	2/3	7	0
	T = 90 °C, t = 72 h, various bases			
Me	1 : 1	(Li_2CO_3)	12	0.20
		(K_2CO_3)	12	0.32
		(Cs_2CO_3)	12	0.25
		(Et_3N)	13	0.12
	Re-treatment of product **7a** with a DS of 0.15			
H	1 : 1	84	12	0.30

Table 2. Sorption of noble metal ions by IMC (DS = 0.23)

Crosslinking agent	Sorption capacity/mmol g^{-1}					
	0.1 *M* HCl			1 *M* HCl		
	Au^{III}	Pt^{IV}	Pd^{II}	Au^{III}	Pt^{IV}	Pd^{II}
Epichlorohydrin	2.4±0.2	1.9±0.1	2.35±0.01	0.18±0.05	0.31±0.07	0.6±0.2
Diglycidyl ether of ethylene glycol	1.9±0.3	1.50±0.04	1.41±0.08	0.53±0.04	0.45±0.08	0.7±0.2
Diglycidyl ether of diethylene glycol	2.0±0.3	1.20±0.05	1.36±0.03	0.88±0.11	0.54±0.04	0.7±0.2

Table 3. Sorption of transition metal ions by IMC (DS = 0.23), pH 5.6, 1 *M* NH_4NO_3

Crosslinking agent	Sorption capacity/mmol g^{-1}			
	Cu^{II}	Ag^{I}	Co^{II}	Ni^{II}
Epichlorohydrin	1.07±0.08	1.9±0.2	0.84±0.02	1.12±0.06
Diglycidyl ether of ethylene glycol	0.20±0.05	1.07±0.07	0.28±0.25	0.18±0.01
Diglycidyl ether of diethylene glycol	0.25±0.07	1.14±0.01	0.16±0.09	0.15±0.05

the products crosslinked with diglycidyl ethers of ethylene glycol and diethylene glycol, the degrees of crosslinking are 25 and 20% and the degrees of swelling are 167 and 148%, respectively. Apparently, the materials crosslinked with these diglycidyl ethers are too rigid to allow free diffusion of metal ions into the matrix; so not all functional groups are involved, which decreases the sorption capacity.

At the same time, an increase in the concentration of HCl dramatically changes the sorption pattern for gold(III) ions extracted with IMC derivatives (Fig. 2). The sorbent obtained with epichlorohydrin as a crosslinking agent is most sensitive to the increasing content of competing chloride ions in solution. As a result, both the sorption capacity and affinity of the sorbent for Au^{III} ions drop sharply. The latter fact is confirmed by an isotherm shape change from high-affinity to low-affinity isotherms when the concentration of HCl in solution increases from 0.1 to 1 mol L^{-1}. It should be emphasized that the sorption capacity drops most substantially in the sorption of both platinum and palladium ions by the epichlorohydrin-crosslinked IMC from 1 *M* HCl (see Table 2).

It is known that the sorption capacity and selectivity of synthetic ion-exchange materials depend on their degree of crosslinking.[28] In our case, the different sorption patterns in the extraction of noble metal ions by crosslinked IMC from low- and high-chloride solutions are most likely due to nonuniform distribution of metal ions between the solution and the polymer. As a result, the concentration of chloride ions (competing with chloroaurate ions for exchange sites) is substantially higher in a strongly swelling polymer and, accordingly, its selectivity and sorption capacity are lower. Obviously, despite their lower sorption capacity, it is rigid matrices crosslinked with diglycidyl ethers that will be more promising for analytical concentration of noble metal ions from acidic high-chloride solutions. Note that the sorption value is virtually independent of the length of the oxyethyl fragment in the diglycidyl ethers used.

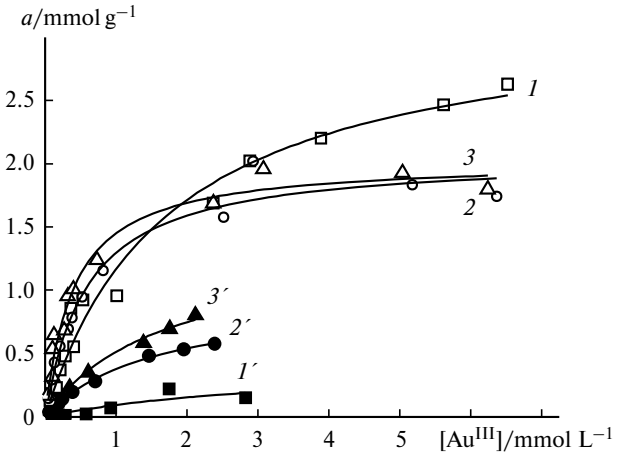


Fig. 2. Sorption isotherms (*a*) of Au^{III} ions on IMC with a DS of 0.23 from 0.1 (*1*—*3*) and 1 *M* HCl (*1′*—*3′*). The sorbents were prepared by crosslinking of polymer **7b** (DS = 0.23) with epichlorohydrin (*1*, *1′*), diglycidyl ether of ethylene glycol (*2*, *2′*), and diglycidyl ether of diethylene glycol (*3*, *3′*).

The character of crosslinking also affects the sorption of transition metal ions: the sorption capacity decreases with an increasing degree of IMC crosslinking (see Table 3). It is worth noting that, in contrast to the anion-exchange sorption mechanism involving chloro complexes of noble metals sorbed on IMC, transition metal ions are sorbed by forming complexes with the amino and imidazolyl groups of IMC. Since complexation with the deprotonated forms of N-ligands is more efficient, pH 3—8 is an optimum range for extraction of transition metal ions. Because the sorption of transition metals at pH < 2 is negligible, noble metal ions can be extracted collectively from complex solutions under these conditions (*i.e.*, their selective extraction with respect to transition metals is ensured).

A number of important facts emerge when comparing the sorption properties of IMC derivatives with those of pyridylethylchitosans.[24] First, the sorption capacity of the poorly substituted IMC (DS = 0.23) for Ag^{I} and Cu^{II} ions is comparable with that of the highly substituted pyridylethylchitosan (DS = 0.83). The sorption capacity of IMC for Ag^{I} ions is higher than that of a synthetic imidazole-containing sorbent (0.47 mmol g^{-1} at pH 5.5).[29] Second, in contrast to pyridylchitosans, the sorption capacity of IMC for Co^{II} and Ni^{II} ions is sufficiently high for materials derived from natural polymers (see Table 3). Although these ions cannot be extracted selectively by IMC from mixtures of transition metal ions, IMC seem to be very promising for purposes not relating immediately with selective extraction of metal ions but requiring a sufficiently high sorption capacity of a polymer for insertion of specific ions into its matrix. Of prime interest is the use of nickel(II) ions for the preparation of catalysts[30] and materials for metal ion affinity chromatography.[31]

Experimental

Chitosan Sonat (DD = 0.84, MW = 250 kDa, ash content 0.19%) was used. The degree of deacetylation (DD) was evaluated by ^{1}H NMR spectroscopy; the molecular weight was determined by viscosimetry as described earlier.[32] Other reagents (Sigma—Aldrich) were used as purchased.

Elemental analysis for C, H, and N was carried out on a Perkin—Elmer automatic analyzer. Diffuse reflection IR spectra were recorded on a Spectrum-One spectrometer (Perkin—Elmer). ^{1}H NMR spectra were recorded on a Bruker DRX-400 spectrometer at 70 °C for higher solubility of samples and better resolution of signals. Samples were dissolved in D_2O/DCl (10 mg mL^{-1}); sodium 3-(trimethylsilyl)propane-1-sulfonate was employed as the internal standard. During ^{1}H NMR experiments, the residual signal of the solvent was suppressed using the presaturation technique.

Model transformations. Methyl 2-acetamido-2-deoxy-α,β-D-glucopyranoside (**2**) and its deacetylated analog (**1**) were prepared as described earlier.[33] The ratio of the α- and β-isomers for compounds **1** and **2** was 4 : 1.

A. A mixture of methyl 2-amino-2-deoxy-α,β-D-glucopyranoside (**1**) (0.193 g, 0.001 mol), 4-methyl-5-imidazolylmethanol hydrochloride (**3**) (0.15 g, 0.001 mol), and Na_2CO_3 (0.212 g, 0.002 mol) in water (2 mL) was kept at 90 °C for 48 h. The residue was evaporated to dryness and the product was extracted with anhydrous ethanol. The extract was evaporated to dryness and analyzed by ^{1}H NMR spectroscopy. ^{1}H NMR (D_2O), δ: 2.20 (s, 3 H, Me, imidazole); 3.22—3.92 (m, 7 H, CH_2, H(2), H(3), H(4), H(5), H(6)); 3.35, 3.41 (both s, 3 H, α-MeO, β-MeO); 3.57 (s, 2 H, NHC$\underline{H}_2$); 4.77 (d, 1 H, H(1), J = 3.6 Hz); 7.59 (s, 1 H, imidazole).

B. An analogous procedure with methyl 2-acetamido-2-deoxy-α,β-D-glucopyranoside (**2**) (0.235 g, 0.001 mol) instead of compound **1** gave the same product as in ***A*** (^{1}H NMR data).

Synthesis of IMC. A mixture of chitosan (**5**) (0.33 g, 0.002 mol), 4(5)-imidazolylmethanol hydrochloride (**6**) (0.26 g, 0.002 mol) or 4-methyl-5-imidazolylmethanol hydrochloride (**3**) (0.30 g, 0.002 mol), and Na_2CO_3 (0.424 g, 0.004 mol) in water (2 mL) as a 12% gel was kept at 90 °C for 84 h. Then the residue was diluted with water (3 mL) and acidified with 34% HCl (0.36 mL). The homogenized solution was precipitated with acetone (100 mL) and the precipitate was separated. The product was extracted with hot ethanol and dried *in vacuo* to a constant weight. The yield was 0.37 g.

The DS values were calculated from the ^{1}H NMR data for compounds **7a,b** by the formula DS = $I_m/(I_m + I_a)$, where I_a and I_m are the integral intensities of the signal for the H(1) atom of the glucopyranose ring containing the unsubstituted and monosubstituted amino group (at δ 4.91 and 5.13, respectively).

Synthesis of sorbents. ***A.*** Epichlorohydrin (0.8 mL) was added to a stirred mixture of IMC (DS = 0.23; 2.1 g), water (100 mL), and NaOH (2.7 g). The reaction mixture was heated at 50 °C for 2 h. The precipitate was filtered off, washed with water until the pH of rinsing water was achieved and the filtrate contained Cl^- ions any more, and dried at 50 °C to a constant weight.

B. A 50% solution of diglycidyl ether of ethylene glycol (3.6 mL) was added to a stirred mixture of IMC (DS = 0.23; 2.1 g) and water (40 mL). The reaction mixture was heated at 60 °C for 3 h. The precipitate was filtered off, washed with water, and dried at 50 °C to a constant weight.

C. The reaction was carried out as described in ***B*** with the exception that diglycidyl ether of diethylene glycol (5.1 g, 50% solution) was used as a crosslinking agent.

The degree of crosslinking was evaluated from elemental analysis data by the formula $\{(C/N)_s - (C/N)_i\}/\{2n\}$, where $(C/N)_s$ and $(C/N)_i$ are the molar ratio of these elements in the crosslinked and initial polymers, respectively; n = 3, 8, and 10 for epichlorohydrin, diglycidyl ether of ethylene glycol, and diglycidyl ether of diethylene glycol, respectively.

The sorption properties of IMC were examined for a 1 : 1000 ratio of the sorbent weight (g) to the volume of the liquid phase (mL) and for a contact time of 18 h. The sorption capacity was calculated from a difference between the initial and equilibrium metal concentrations determined in solution by atomic absorption spectrometry (Solaar M6 instrument, Thermo, USA).

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